COAGULATION AND SEDIMENTATION WITH CHEMICALS[1]

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Coagulation and sedimentation with chemicals, followed by rapid filtration through sand filters, have become the generally adopted methods of purifying the public water supplies in the United States. Even where the softening of a water supply comprises the principal portion of the process, coagulation, sedimentation and filtration are important factors in the final cleansing of the water. The method of applying the chemicals and the effects they produce are, therefore, of the greatest significance.

If the phenomena accompanying the processes of coagulation and sedimentation are carefully studied, it soon becomes evident that we are dealing with chemical reactions on a large scale, and that the physical changes brought about by these reactions are governed by principles and laws which have been investigated by scientists within comparatively recent years, and classified by them under the names of physical and colloidal chemistry. The phenomena are complex and by no means entirely understood in all of their ramifications. The object of the present paper is to outline and classify the various factors entering into the processes of water purification without going too deeply into details. The practical value of understanding the main features of these processes, in relation to the design of the structures in which they occur, is obvious, and at least may justify the effort to set forth in an orderly manner the changes that take place.

Excluding for the time being those phases of the problem which relate to water softening, let us consider those which have to do with purification by clarification, that is, with the removal of suspended impurities. In natural waters used for public supplies, there are usually found both inorganic and organic matter which are not in

solution, but which are in an extremely finely divided state. Some of this material does not readily settle out, even when the water is quiescent. Some of the organic matter appears to be in actual solution, although it has been discovered that this is not always the case. Such material will not precipitate unless the size of the particles of which it is composed is enlarged, or is trapped by other material which is collecting into larger masses and thus becomes capable of being deposited by sedimentation.

The impurities referred to in the above paragraph consist chiefly of inorganic compounds or mixtures commonly known as clay and silt, and of organic matter, both dead and living. In the dead organic matter may be found nitrogenous and carbonaceous compounds, and in the living matter, bacteria and microscopic plant and animal forms. Much of the inorganic material is in that finely divided condition known as the colloidal state of matter. The dead organic matter is usually in this condition, while the cells of the living organic matter may be always considered as in this form.

Since a portion of the suspended impurities are, on account of their extraordinarily small size, not capable of settling out unaided, it becomes necessary to add something to the water which will cause these particles to come together. The aggregation of these particles into masses of such size that they may settle out is commonly known as coagulation. This process is usually effected through the agency of a chemical compound such as aluminum sulphate or ferrous sulphate, which, in reacting with the natural alkalinity of the water or with an alkalinity created by the addition of lime or soda ash, produces a colloidal precipitate. The latter by reason of the electrical charges upon its particles, which are of opposite sign from those on most of the natural colloidal impurities, brings about coagulation of the suspended matter, and subsequently is settled out under proper conditions.

From the above it is evident that there first occurs one or more chemical reactions followed by certain physical changes. It is this actual division of the process into two parts to which attention should be directed, if the full significance of the phenomena involved is to be understood. The reaction between the sulphate of aluminum and the alkali in the water is the usual exchange of ions, whereby an insoluble or practically insoluble product is one of the results of the reaction. Every precipitation is preceded by a state of supersaturation with respect to the precipitated solid, and after it is complete, the liquid

is saturated with it, i.e., it is in equilibrium with the liquid. The establishing of this equilibrium may require considerable time, and depends entirely upon the properties of the compound resulting from the chemical reaction, and from the physical and chemical characteristics of the water in which the reaction takes place.

It is necessary, therefore, to realize that a chemical reaction or series of reactions precedes changes which establish physical equilibrium. The velocity of most chemical reactions, at least of those commonly met with in water purification, is extremely high, in fact too high to be able properly to measure the time in which they occur. The higher the temperature, the more rapid are the ionic exchanges. If more than one reaction is necessary, as in the case of ferrous sulphate and lime, or lime and soda ash in water softening, probably a somewhat longer time is needed, but even here the chemical reactions practically complete themselves in an immeasurably short space of time.

The foregoing statement is true only if the reacting substances are in solution. The velocity of a reaction is directly proportional to the concentration of each reacting constituent, and is understood to be the ratio between the amounts of the transformed substances and the time required for transforming them. The greatest velocity-value is at the beginning of the reaction, and becomes less and less as the reaction proceeds, and leads to the theoretical result that the reaction is only complete after an infinite length of time. But while this may be absolutely true, for practical purposes any residual action may be regarded as non-measureable after ten times the period which is required to complete the first half of the reaction.[3] Since for homogeneous mixtures of reacting solutions of the general character used in coagulating a water, the velocity of the reaction at the start is very high, it follows that the reacting quantities in the residual action are practically negligible. However, in non-homogeneous mixtures, such as occur when feeding milk of lime, or dry feeding of hydrated lime, aluminum sulphate or even sulphate of iron, true solution of these reagents must precede reaction, and hence the actual or practical completion of the reaction may take a sensible period of time.

The second part of the phenomena, that is, the adjustment of the solid phases of the products of the reaction to the liquid, requires

[3] Foundations of Analytical Chemistry, Wm. Ostwald.

more or less time. As all precipitates are probably at first in a colloidal form, as previously stated, and as the speed with which they pass through this stage depends upon several factors which differ with the different chemicals employed, it is evident that each case will require more or less special consideration.

When aluminum hydroxide is one of the reaction products, there are comparatively few complications. It is a relatively insoluble compound, and the carbon dioxide formed at the same time appears to have no inhibiting effect. Slow coagulation, therefore, may be due to protective colloids naturally present in the water, to lack of negatively charged colloidal particles to neutralize the positively charged particles of aluminum hydroxide, to very low temperatures, or to insufficient movement of the water to facilitate contact of suspended particles.

In the case of ferrous sulphate, its decomposition first produces ferrous bicarbonate, which, because of its instability and because of the lime always added with the iron sulphate, is quickly converted into ferrous hydroxide and calcium carbonate. The oxygen dissolved in the water rapidly oxidizes the ferrous iron to the ferric condition, and there is finally produced ferric hydroxide, or the coagulating compound desired. Here there are a series of reactions followed by the usual phenomena of matter in the colloidal condition.

In the softening of water with lime and soda ash, the ionic exchanges between the CO_3, HCO_3, SO_4, Ca and Mg ions constitute a series of chemical reactions intermingled with physical changes, which require more or less time for their completion. Calcium carbonate comes down first in an amorphous form, and in this state is perceptibly soluble in the water. The amorphous form gradually changes to the crystalline (assuming the rhombohedral forms of calc spar) which is much more insoluble in the water. Magnesium carbonate is very soluble in water, and even the hydroxide is relatively soluble unless an increased concentration of hydroxyl ions, produced by adding an excess of alkali (CaO_2H_2 or $NaOH$), decreases its solubility sufficiently to cause most of it to settle out.

In water softening considerable masses of deposited sludge are usually in contact with the water during the purification process. Since equilibrium must be established between the water (which is supersaturated at the beginning of the process, with respect to the precipitated solids), and the precipitate, it follows that intimate contact of the sludge with the liquid will hasten the change from a state

of supersaturation to one of saturation, which latter is the stable con-
dition desired.   This change is hastened by exposure of large areas
of the precipitate to the liquid and by agitation.   The practical
significance of these conditions is apparent, since by thorough and
rapid mixing of the reacting substances in solution, surface contact
of the liquid with the precipitate, and agitation of the mixture, we
bring about as complete a separation as it is possible to produce.

If we now consider the physical changes in themselves, which, as
has been explained, must follow the chemical reactions, it is evident
that the phenomena are practically all related to matter in the col-
loidal state.   For example, Mr. J. F. Norton concisely sums up the
colloidal reactions when aluminum sulphate is applied to natural
waters as a coagulant, as follows:

> First, there is formation of a positively charged colloidal hydroxide.
> Second, this hydroxide reacts with the negatively charged bacteria and clay
> or other colloids.   Third, the excess colloidal aluminum hydroxide is pre-
> cipitated by agitation.   Fourth, the positively charged coloring matter is
> precipitated by the negatively charged sulphate ion.   Fifth, any color in
> true solution is adsorbed by the hydroxide.[4]

The mutual precipitation of oppositely charged colloidal particles
appears to be the basis upon which most of the coagulation processes
depend.   It has been noted that the effect of an electrolyte upon a
suspensoid is first of all to diminish the potential difference betwen the
disperse phase and the medium, and precipitation only occurs when
the potential difference has been brought sufficiently near to zero, the
point of electric neutrality or the iso-electric point.   A definite con-
centration of the electrolyte is evidently necessary for precipitation;
and as smaller concentrations may cause only partial precipitation or
even none at all, it is not improbable that larger concentrations may
also produce partial or no precipitation.   The analogy suggested
between these principles and the facts well-known to operators of
purification plants is worth noting.   For example, it is almost always
true that there is a minimum quantity of coagulant below which the
most imperfect and unsatisfactory coagulation is obtained.   Catlett
several years ago found that a both highly colored and turbid water,
which was a mixture of two waters which reached the filter plant
before sufficient time had elapsed for mutual precipitation of the
colloids, required the addition of alkali before the alum would pre-

[4] The Chemistry of Colloids, Zsigmondy, Spear and Norton.

cipitate. The color was not completely removed even then. By adding an excess of alum first, which gave an opportunity for the aluminum and sulphate ions both to act, and then introducing the alkali so that aluminum hydroxide would be formed, a satisfactory coagulation resulted with a much smaller quantity of the coagulant.[5]

The protective action of certain colloids in preventing coagulation is illustrated by the fact that a water containing considerable sewage requires more alum for purification than an unpolluted water having the same turbidity and color. The fact established by colloidal chemists, that by adding a reagent slowly to a colloidal solution more is required to produce precipitation than if added rapidly, may afford a possible explanation for some of the poor results obtained in some purification plants. The phenomena of adsorption, depending as it does principally upon the factor of "surface concentration," that is, upon the difference of concentration at the boundary between two heterogeneous phases, whether the phases be gas, liquid or solid, may account for many of the obscure and puzzling phenomena of the sand filtration of coagulated waters.

Like all new developments in science, colloidal chemistry has been seized upon to explain many phenomena which are complex, and which will eventually be found to require the formulation of entirely new and unrelated principles. If investigators, however, will bear in mind, that from the mass of facts, concerning the colloidal state of matter, principles and laws are slowly being developed and by use of which explanations of some of the obscure phenomena in coagulation, sedimentation and filtration of water, may be found, there may be a real advance in the art of water purification.

[5] *Engineering Record*, 73, 741 (1916).